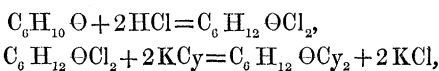
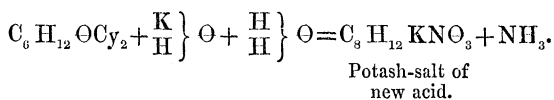


When acetone is saturated with hydrochloric acid, several condensed compounds are formed, which remain in union with the acid. The question now arises, which of these compounds generate the acid we have just been studying? and which the neutral body? In the hope of determining this point, I prepared the two most important of these compounds in a state of purity, namely oxide of mesityle and phoron, and saturated them with hydrochloric acid gas. After the lapse of twelve hours the two saturated bodies were well washed with water, and treated separately with cyanide of potassium and caustic potash in the manner I have just described. The results were decisive. The mesityle compound yielded the acid, and the phoron compound the neutral body. The following equations will explain the formation of the acid:—



and



It will be observed that only one of the cyanogen atoms is transformed into C O O K.

The foregoing derivatives of acetone are, I think, in many respects very remarkable bodies. I therefore propose to submit them to a careful study. I propose also to ascertain whether or not the true aldehydes yield analogous bodies when treated in a similar manner.

III. "Researches on the Hydrocarbons of the Series C_n H_{2n+2}.—
No. IV." By C. SCHORLEMMER. Communicated by Prof. G.
G. STOKES. Received April 13, 1868.

On the relation between Boiling-point and Chemical Structure.

It is from researches published only during last year that we have obtained a more definite knowledge of the chemical structure of some of the hydrocarbons of the above series, so that we are enabled to explain the mode in which the carbon atoms are united. This has been achieved by obtaining these hydrocarbons by synthesis from other compounds, the structure of which is perfectly well known.

Thus Friedel and Ladenburg* prepared, by acting upon methylchloracetol, C $\left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3, \\ \text{Cl}_2 \end{array} \right.$ with zincethyl, the hydrocarbon C₇H₁₆, which they call

carbdimethyldiethyl, and which has the structure C $\left\{ \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{C}_2\text{H}_5, \\ \text{C}_2\text{H}_5 \end{array} \right.$ Butlerow†

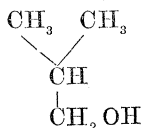
* Ann. der Chem. und Pharm. vol. cxlii. p. 310.

† Ibid. vol. cxliv. p. 10.

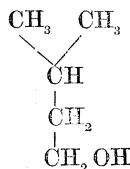
replaced in tertiary butyl alcohol the group HO by hydrogen, and obtained an isomer of diethyl to which he gives the name trimethylformen,

$\text{C} \begin{cases} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \\ \text{H} \end{cases}$. In my last communication to the Society I described di-isopropyl and amylisopropyl, and pointed out their constitution*. Further, Erlenmeyer has shown that amyl alcohol and butyl alcohol formed by fermentation have the following structure†:—

Butyl alcohol.



Amyl alcohol

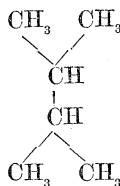


These two compounds contain, therefore, the group isopropyl, $\text{CH}(\text{CH}_3)_2$, which also must be present in the hydrocarbons derived from these alcohols.

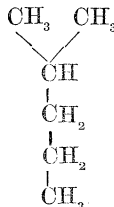
All hydrocarbons of known structure may be arranged in four groups; the members of each group, which are liquids at the mean temperature of the air, exhibit a very regular increase in the boiling-point for each increase of CH_2 .

1st. group. Hydrocarbons in which each atom of carbon is united with not more than two other carbon atoms, or in which the carbon atoms are arranged in a single chain.—To this group belong the three lowest members of the series $\text{C}_n \text{H}_{2n+2}$, of which no isomers exist, as well as diethyl, $\text{C}_4 \text{H}_{10}$, hexylhydride, $\text{C}_6 \text{H}_{14}$, derived from suberic acid‡, and heptylhdyride, $\text{C}_7 \text{H}_{16}$, from azelic acid§. My reasons for considering that the two last ones belong to this group are: (1) They boil at a higher temperature than their isomers of known structure; and we find that the simpler the manner in which the carbon atoms are combined, the higher the boiling-point. Thus we have,—

Di-isopropyl boils at 58° C.



Ethylbutyl boils at 62° C.



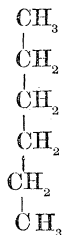
* Proc. Roy. Soc. vol. xvi. p. 34.

† Journ. Chem. Soc. N. S., vol. ii. p. 260.

‡ Zeitschrift für Chemie, vol. iii. p. 117.

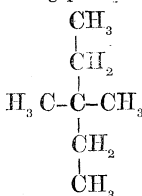
§ Proc. Roy. Soc. vol. xiv. p. 464.

Now hexylhydride boils at $69^{\circ} \cdot 5$ C., and the only structure more simple than ethylbutyl is the following, which must express that of hexylhydride,

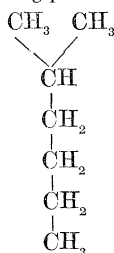


The same is the case in the hydrocarbons having the composition $C_7 H_{16}$,—

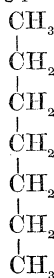
Carbdimethyldiethyl.
Boiling-point 86° .



Ethylamyl.
Boiling-point 91° .



Heptylhdyride.
Boiling-point $100^{\circ} \cdot 5$.



(2) The formation of these hydrocarbons points out that they must have a very simple constitution. The acids from which they are derived are obtained by the splitting up of compounds containing a large number of carbon atoms, and from these acids they (hydrocarbons) are derived by a further separation of carbon. The difference in the boiling-points of hexylhydride and heptylhdyride is 31° C.

Boiling-point.

$C_6 H_{14}$		$69^{\circ} \cdot 5$
$C_7 H_{16}$		$100^{\circ} \cdot 5$

The hydrocarbon $C_6 H_{14}$, found in American petroleum appears to be identical with that prepared from suberic acid. The higher specific gravity which the hexylhydride from rock-oil shows, as observed by Cahours and Pelouze and by me, is occasioned by impurities. As I have shortly mentioned in my last communication, I have studied the action of nitric acid upon this hydrocarbon. On oxidizing in this way about 120 grms., of which the boiling-point was 67° to 69° and the specific gravity $0 \cdot 6709$, at 15° , about 10 grms. were left unattacked, which certainly must have been very pure. This remaining portion boiled at 70° , and had the specific gravity $0 \cdot 6651$ at $16^{\circ} \cdot 5$. The hexylhydride which Erlenmeyer and

Wanklyn prepared from mannite* also exhibits in its boiling-point and specific gravity a close agreement with the hydrocarbon from suberic acid, and appears to be the same,—

	Boiling-point.	Spec. grav.
C_6H_{14} from suberic acid	$69^{\circ}5$	0·6617 at $17^{\circ}5$
„ „ mannite	68-70	0·6645 at $16^{\circ}5$
„ „ rock-oil	70	0·6651 at $16^{\circ}5$

2nd group. Hydrocarbons in which one atom of carbon is united with three others, or which contain the group isopropyl. —The members of this section are trimethylformen, amylhydride, ethylbutyl, ethylamyl, and the hydrocarbon C_8H_{18} which I have prepared from the caprylalcohol, obtained from castor oil†. Trimethylformen boils at about $-15^{\circ}C$.; the other members are liquid at common temperature, and show the same difference in their boiling-points as those of the first group, namely 31° .

		Boiling-point.	
		Observed.	Calculated.
Amylhydride, C_5H_{12}	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array} $	30°	30°
Ethylbutyl, C_6H_{14}	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array} $	62°	61°
Ethylamyl, .. C_7H_{14}	$ \begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \diagdown \quad \diagup \\ \text{CH} \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array} $	91°	92°

* Journ. Chem. Soc. N. S. vol. i. p. 233.

† This alcohol is, as I have found, a secondary or iso-alcohol. An account of this investigation, and the reasons why I class the hydrocarbon derived from the alcohol in the above group, I shall communicate to the Society shortly.

		Boiling-point.	
		Observed.	Calculated.
Octylhydride, $C_8 H_{18}$ (from caprylalcohol)	$ \begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ CH \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_3 \end{array} $	124°	123°

3rd group. Hydrocarbons which contain the group isopropyl twice.—The difference in the boiling-points of the members of this group is 25° C. They are di-isopropyl, dibutyl, which, as I have shown, is identical with amylisopropyl, butylamyl, and diamyl.

Di-isopropyl, $C_6 H_{14}$	$ \begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ CH \\ \\ CH \\ \diagdown \quad \diagup \\ CH_3 \quad CH_3 \end{array} $	58°	58°
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(Not known) $C_7 H_{16}$	—	—	83°
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Dibutylamyl, } isopropyl. }	$ \begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ CH \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH \\ \diagdown \quad \diagup \\ CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ CH \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_2 \\ \diagdown \quad \diagup \\ CH_3 \quad CH_3 \end{array} $	109	108°
Butylamyl .. $C_9 H_{20}$	$ \begin{array}{c} CH_2 \\ \\ CH_2 \\ \\ CH_2 \\ \diagdown \quad \diagup \\ CH_3 \quad CH_3 \end{array} $	132°	133°

		Boiling-point.	
		Observed.	Calculated.
Diamyl	$\dots C_{10} H_{22} =$ $ \begin{array}{c} CH_3 \quad CH_3 \\ \diagdown \quad \diagup \\ CH \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH_2 \\ \\ CH \\ / \quad \backslash \\ CH_3 \quad CH_3 \end{array} $	158°	158°

4th group. Hydrocarbons in which one atom of carbon is combined with four other carbon atoms.—Of this group only one member is known, namely carbdimethyldiethyl, which boils at 86°.

It thus appears that from the boiling-point of a hydrocarbon of the series $C_n H_{2n+2}$ conclusions may be drawn concerning its constitution, just as in the series of aromatic hydrocarbons*. Further researches must show whether the law which I have pointed out in this paper is a general one.

IV. "Researches on the Hydrocarbons of the Series $C_n H_{2n+2}$ —No. V." By C. SCHORLEMMER. Communicated by Professor G. G. STOKES, Sec. R.S. Received May 7, 1865.

Oxidation Products.

In a former communication† I have shortly described the action of different oxidizing agents upon some of the saturated hydrocarbons; the following paper contains some further results which I have since then obtained. One of the most striking properties of these compounds is, that they are with the greatest difficulty acted upon by any oxidizing substance in the cold. On heating them, however, a reaction sets in, and either they are completely burnt up to carbonic dioxide and water, or other oxidation products besides those two are formed in comparatively small quantities; thus chromic acid produces some acetic acid. Fuming nitric acid, which in the cold shows no action whatever, even if left in contact with one of these hydrocarbons for months, acts rather violently on gently heating; acid of the specific gravity 1·4 acts in a similar way, and produces the same products, but the reaction is much less violent. The apparatus which I

* Compare, about the boiling-points of the aromatic hydrocarbons, the elaborate paper of Kopp in *Ann. der Chem. und Pharm.* vol. v. (Supplement) p. 315.

† Proceedings of the Royal Society, vol. xvi. p. 38.